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## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

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 Office, PCT  
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 Arlington, VA 22202  
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 in its capacity as elected Office

Date of mailing (day/month/year) 23 November 2000 (23.11.00)	
International application No. PCT/EP00/03724	Applicant's or agent's file reference C3913(C)/rkk
International filing date (day/month/year) 20 April 2000 (20.04.00)	Priority date (day/month/year) 30 April 1999 (30.04.99)
Applicant FRASER, Stuart, Bernard	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
 27 October 2000 (27.10.00)

☐ in a notice effecting later election filed with the International Bureau on:  
 \_\_\_\_\_

2. The election ☒ was  
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Charlotte ENGER Telephone No.: (41-22) 338.83.38
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# INTERNATIONAL SEARCH REPORT

Inventor's Application No:  
PCT/EP 00/03724

A. CLASSIFICATION OF SUBJECT MATTER  
C11D17/00,3/50,1/62

According to International Patent Classification (IPC) or to both national classification and IPC?

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 19751151 A1 (HENKEL KGaA) 20 May 1999, page 2, lines 51-60, page 4, lines 56-64, claim 1.	1-4, 6, 8, 9, 12-14
X, P	-- WO 00/06690 A1 (COLGATE-PALMOLIVE COMPANY) 10 February 2000, abstract, claims 1,3-6,13-15.	1-4, 6, 8, 9, 12-14
A	-- US 5447644 A (GUENIN et al.) 05 September 1995, the whole document.	1-4, 6, 8, 9, 12-14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "&" document member of the same patent family

Date of the actual completion of the international search  
30 August 2000

Date of mailing of the international search report  
13. 10. 2000

Name and mailing address of the ISA

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**ANHANG**

Zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

**ANNEX**

To the International Search Report to the international Patent Application No.

**ANNEXE**

Au rapport de recherche international relatif à la demande de brevet international n°

PCT/EP 00/03724 SAE 286109

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

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Im Recherchenbericht angeführte Patentdokumente Patent document cited in search report Document de brevet cité dans le rapport de recherche			Datum der Veröffentlichung Publication date Date de publication		Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets		Datum der Veröffentlichung Publication date Date de publication	
DE	A1	19751151	20-05-1999		EP	A1	1032626	06-09-2000
					WO	A1	9925797	27-05-1999
WO	A1	00006690	10-02-2000		AU	A1	52458/99	21-02-2000
US	A	5447644	05-09-1995		CA	AA	2148675	13-11-1995
					EP	A2	682104	15-11-1995

*FOR THE PURPOSES OF INFORMATION ONLY*

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## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference C3913(C)/rkk	FOR FURTHER ACTION <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. PCT/EP 00/03724	International filing date (day/month/year) 20 April 2000	(Earliest) Priority Date (day/month/year) 30 April 1999
Applicant UNILEVER HOUSE et al.		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. ☐ Certain claims were found unsearchable (see Box I).
2. ☐ Unity of invention is lacking (see Box II).
3. ☐ The international application contains disclosure of a nucleotide and/or amino acid sequence listing and the international search was carried out on the basis of the sequence listing
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4. With regard to the title, ☒ the text is approved as submitted by the applicant.
  - ☐ the text has been established by this Authority to read as follows:
5. With regard to the abstract,
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6. The figure of the drawings to be published with the abstract is:
  - Figure No.            ☐ as suggested by the applicant.
  - ☐ because the applicant failed to suggest a figure.
  - ☐ because this figure better characterizes the invention.
  - ☒ None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No:  
PCT/EP 00/03724

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X, P	WO 00/06690 A1 (COLGATE-PALMOLIVE COMPANY) 10 February 2000, abstract, claims 1, 3-6, 13-15. --	1-4, 6, 8, 9, 12-14
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Date of the actual completion of the international search

30 August 2000

Date of mailing of the international search report

13. 10. 2000

Name and mailing address of the ISA

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**ANHANG**

Zum internationalen Recherch  
richt über die internationale Patent-  
anmeldung Nr.

**ANNEX**

To the International Search  
Report to the international Patent  
Application No.

**ANNEXE**

Au rapport de recherche inter-  
national relatif à la demande de  
brevet international n°

PCT/EP 00/03724 SAE 286109

In diesem Anhang sind die Mitglieder der  
Patentfamilien der im obengenannten  
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Im Recherchenbericht angeführte Patentedokumente Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
DE A1 19751151	20-05-1999	EP A1 1032626	06-09-2000
		WO A1 9925797	27-05-1999
WO A1 00006690	10-02-2000	AU A1 52458/99	21-02-2000
US A 5447644	05-09-1995	CA AA 2148675	13-11-1995
		EP A2 682104	15-11-1995

C3913

German OLS 197 51 151 A1

Application filed: 19.11.97

OLS published: 20.5. 99

Henkel KGaA

**Clear fabric-softeners with micro-emulsified perfume oils**

Clear aqueous fabric softeners with outstanding storage stability and excellent fragrancing properties contain from 2 to 60% by weight of a reaction product of trialkanolamines with a mixture of fatty acids and dicarboxylic acids, optionally alkoxyated and subsequently quaternised in the known manner, from 0.5 to 20% by weight of a perfume oil micro-emulsion having a droplet size of from 10 to 100 nm itself containing from 10 to 50% by weight of perfume oil, from 1 to 10% by weight of an oil co-component, from 1 to 30% by weight of an emulsifier of the alkylpolyglycoside type and optionally up to 10% by weight of a nonionic or cationic co-emulsifier, the weight ratio of perfume oil to oil co-component being from 10:1 to 2:1, and water or an aqueous solution of other active agents or adjuncts to balance.

**Description**

This invention relates to clear aqueous perfume-containing softeners of low to high concentration for softening fabrics. In particular the invention relates to clear aqueous softeners that are suitable for use in the rinse cycle of a domestic washing machine and which impart excellent softness, antistatic properties, easy-iron properties, good rewettability and a long-lasting pleasant fragrance to fabrics treated therewith.

Softener compositions for use in the rinse cycle are extensively described in the art. These compositions usually contain as the active material a cationic quaternary ammonium compound which is dispersed in water. Depending on the content of active material present in the finished softener compositions, these are classed either as dilute ready-to-use products (active material contents less than 7% by weight) or as concentrates (active material contents more than 7% by weight). Because of the small volume and hence reduced packaging and

transport costs, fabric softener concentrates have ecological advantages and have become increasingly popular commercially. Because they contain cationic compounds which have only limited water-solubility, conventional softener compositions are dispersions, have a milky appearance and are not translucent. For aesthetic reasons it can however be desirable to offer consumers translucent, clear softeners which are visually distinct from known products.

The manufacture of clear fabric-softeners and the problems associated with their production are also extensively described in the art. For example European patent application EP-A-0 404 471 (Unilever) describes isotropic liquid fabric softener compositions with at least 20% by weight of softener and at least 5% by weight of a short-chain organic acid.

Clear fabric softener compositions with a large solvent content are also known, the softening materials used in these products being for example quaternised ester ammonium compounds ("ester quats") with unsaturated, branched or short-chain alkyl groups. Such systems have the disadvantage that they can form lumps that are attracted to fibres, where they cause spots and reduced softness. The storage and low-temperature stability of these products is also often unsatisfactory, with the result that they thicken or are subject to precipitation or phase separation at between 18 °C and 4 °C.

To overcome these problems, WO 97/03169 (Procter & Gamble) proposes the use of less than 40% by weight of solvents which have a ClogP value of between 0.15 and 0.64. The active materials described in this document have unsaturated or relatively short (C<sub>12-14</sub>) alkyl chains and are contained in the compositions in amounts of from 2 to 80% by weight, preferably from 13 to 75% by weight and in particular from 17 to 70% by weight. In order to obtain clear softeners with from 2 to 10% by weight of active material it is necessary to use a special manufacturing process requiring a premix of ester quat, solvents and perfume has to be used, because otherwise the compositions will remain opaque.

Novel ester quats are described in DE 195 39 846 (Henkel). The cationic surfactants described therein are the reaction products of triethanolamine with mixtures of fatty acids and

dicarboxylic acids. Applications for these novel substances mentioned in the specification are hair conditioners, shampoos, shower gels and washing lotions. These novel ester quats are prepared by reacting trialkanolamines with a mixture of fatty acids and dicarboxylic acids, preferably in a mole ratio of from 1:10 to 10:1 and quaternising the resulting esters in the usual manner.

The use of the ester quats described in DE 195 39 846 C1 to produce water-clear softeners is described in Research Disclosure May 1997, No. 39729 (disclosed anonymously). This research disclosure discloses user concentrations for the ester quats of between 5 and 15% by weight. The specification is silent as regards the fragrancing of these products.

In the case of all the clear fabric-softeners and processes for their manufacture that are described in the art, the production of low-concentration products is more costly than the production of concentrates. In addition, the incorporation of fragrances can cause considerable problems because many perfumes do not dissolve in the formulations, or separate out again after a short period of time. The incorporation of emulsifiers in clear products before perfumes are added does not solve this problem satisfactorily because high emulsifier concentrations are needed if storage stability is to be acceptable.

Perfume concentrates in the form of transparent aqueous microemulsions are described in earlier German patent application DE 196 24 051.4 (Henkel). The microemulsions disclosed therein contain from 10 to 50% by weight of perfume oil, from 1 to 10% by weight of an oil co-component, from 1 to 30% by weight of an emulsifier of the alkylpolyglycoside type, as well as optionally up to 10% by weight of a nonionic or cationic co-emulsifier, and they have particle sizes of between 10 and 100 nm, the weight ratio of perfume oil to oil co-component being from 10:1 to 2:1.

The object of the present invention was therefore to provide clear, perfume-containing aqueous softeners of low to high concentration for softening fabrics which did not exhibit the above problems. In particular, it was an object of the invention to provide clear fabric softeners which had outstanding storage stability even without the use of high emulsifier

concentrations, and which in addition were characterised by outstanding fragrancing properties.

It has now been found that clear perfume-containing softeners of low to high concentration can be obtained with the ester quats described in DE 195 39 846 if the perfume is incorporated as a perfume oil micro-emulsion.

The invention relates to a clear, aqueous softener containing - calculated on the total composition -

- a) from 2 to 60% by weight of a reaction product of trialkanolamines with a mixture of fatty acids and dicarboxylic acids, the reaction product being optionally alkoxylated and thereafter quaternised in the known manner,
- b) from 0.5 to 20% by weight of a perfume oil microemulsion with a droplet size between 10 and 100 nm, itself containing from 10 to 50% by weight of perfume oil, from 1 to 10% by weight of an oil co-component, from 1 to 30% by weight of an emulsifier of the alkyl polyglycoside type, and optionally up to 10% by weight of a nonionic or cationic co-emulsifier, the weight ratio of perfume oil to oil co-component being from 10:1 to 2:1, and
- c) water or an aqueous solution of other active materials and adjuncts to balance.

The clear aqueous softener of the invention contains ester quats as the fabric-softening active material. While there are a considerable number of possible compounds in this class, the ester quats used in the invention are obtained by reacting trialkanolamines with a mixture of fatty acids and dicarboxylic acids, then optionally alkoxylating the reaction product and quaternising it in the known manner, as described in DE 195 39 846.

The ester quats that are thereby obtained in this manner are outstandingly useful for the preparation of clear, aqueous softeners of low to high concentration which together with a perfume oil microemulsion and optionally other components furnish clear, storage-stable and extremely effective perfumed fabric softeners in accordance with the invention. Because a great number of suitable products can be obtained depending on which trialkanolamine, fatty acids, dicarboxylic acids and quaternising agent are selected, a description of the ester quats

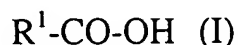
that are used in the invention in terms of the route by which they are prepared provides more specific information than does a general formula.

The stated components which react with one another to give the ester quats that are to be used in accordance with the invention can be used in varying quantitative ratios. In the present invention clear softeners are preferred which contain from 2 to 60, preferably from 3 to 35 and in particular from 5 to 30% by weight of a reaction product of alkanolamines with a mixture of fatty acids and dicarboxylic acids in a mole ratio of from 1:10 to 10:1 and preferably from 1:5 to 5:1 which has optionally been alkoxylated and thereafter quaternised in the known manner. Especially preferred is the use of triethanolamine, so that further preferred clear softeners of the present invention contain from 2 to 60, preferably from 3 to 35 and in particular from 5 to 30% by weight of a reaction product of triethanolamine with a mixture of fatty acids and dicarboxylic acids in a mole ratio of from 1:10 to 10:1 and from 1:5 to 5:1 which has optionally been alkoxylated and quaternised in the known manner.

As fatty acids there can be used in the reaction mixture for the ester quats any acids obtained from vegetable or animal oils and fats. Fatty acids that are not solid at room temperature, for example that are pastes or liquids, can also be used in the reaction mixture. Irrespective of their physical state, the fatty acids can also be saturated or mono to polyunsaturated.

Naturally, it is possible to use not only "pure" fatty acids but also technical-grade fatty acid mixtures obtained from oil and fat-splitting, these mixtures being distinctly preferred for economic reasons. For example the reaction mixtures used to prepare ester quats for the clear aqueous softeners of the invention can contain single species or mixtures of the following acids: caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, octadecan-12-olic acid (*sic*), arachic acid, behenic acid, lignoceric acid, cerotic acid, melissic acid, 10-undecenoic acid, petroselinic acid, petroselaidic acid, oleic acid, elaidic acid, ricinoleic acid, linolaidic acid,  $\alpha$  and  $\beta$ -elaëostearic acid, gadoleic acid, erucic acid, brassidic acid. Naturally, fatty acids with an odd number of C atoms can also be used, for example undecanoic acid, tridecanoic acid, pentadecanoic acid, heptadecanoic acid, nonadecanoic acid, heneicosanoic acid, tricosanoic acid, pentacosanoic acid, and heptacosanoic acid.

In the present invention it is preferred to use fatty acids of formula I in the reaction mixture employed for the preparation of the ester quats, with the result that preferred clear softeners contain a reaction product of trialkanolamines with a mixture of fatty acids of formula I



wherein  $R^1\text{-CO-}$  is an aliphatic, linear or branched acyl group with from 6 to 22 carbon atoms and 0 and/or 1, 2 or 3 double bonds and dicarboxylic acids in a mole ratio of from 1:10 to 10:1 and preferably from 1:5 to 5:1, which product is optionally alkoxyated and thereafter quaternised in the known manner, in an amount of from 2 to 60, preferably from 3 to 35 and in particular from 5 to 30% by weight.

As dicarboxylic acids that are useful for the preparation of the ester quats used in the compositions of the invention there can be used in particular saturated or mono or polyunsaturated  $\alpha,\omega$ -dicarboxylic acids. As examples, mention can be made of the saturated species oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanoic<sup>1</sup> and dodecanoic<sup>1</sup> acid, brassylic acid, tetra and pentadecanoic<sup>1</sup> acid, thapsic acid, as well as hepta, octa, and nonadecanoic<sup>1</sup> acids, eicosanoic and heneicosanoic acid and phellogenic acid. Preferably there are used in the reaction mixture dicarboxylic acids that conform to Formula II, so that there are preferred clear softeners that contain, in amounts of from 2 to 60, preferably from 3 to 35 and in particular from 5 to 30% by weight, a reaction product of trialkanolamines with a mixture of fatty acids and dicarboxylic acids of formula II

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<sup>1</sup> *Translator's note:* Sic. Do they mean the dioic acids?



wherein X represents an optionally hydroxy-substituted alkenyl group with from 1 to 10 carbon atoms, in a mole ratio of from 1:10 to 10:1 and preferably from 1:5 to 5:1, which product can optionally be alkoxylated and thereafter quaternised in the known manner.

Of the large number of ester quats that can be prepared and used in the invention, especially useful compounds are those where the alkanolamine is triethanolamine and the dicarboxylic acid is adipic acid. Thus there are especially preferred herein clear softeners that contain, in an amount of from 2 to 60, preferably from 3 to 35 and in particular from 5 to 30% by weight, a reaction product of triethanolamine with a mixture of fatty acids and adipic acid in a mole ratio of from 1:5 to 5:1, preferably from 1:3 to 3:1 which product was subsequently quaternised in the known manner.

The perfume oil microemulsions used in the compositions of the invention which provide intense fragrancing and fragrance transfer to treated fabrics without a loss in product transparency have particle sizes of between 10 and 100 nm and contain from 10 to 50% by weight of perfume oil, from 1 to 10% by weight of an oil co-component, from 1 to 30% by weight of an emulsifier of the alkylpolyglycoside type and optionally up to 10% by weight of a nonionic or cationic co-emulsifier, the weight ratio of perfume oil to oil co-component being from 10:1 to 2:1.

As perfume oils and fragrances there can be used individual perfume compounds, for example synthetic products in the class of esters, ethers, aldehydes, ketones, alcohols and hydrocarbons. However, mixtures of different perfume compounds are preferred which together produce an attractive fragrance note. Such perfume oils can also contain natural perfume mixtures such as those that can be obtained from plant sources, for example pine, citrus, jasmine, patchouli, rose, or ylang-ylang oil. Also useful are clary sage oil, camomile oil, clove oil, melissa oil, mint oil, cinnamon leaf oil, lime blossom oil, juniper berry oil, vetiver oil, olibanum oil, galbanum oil, and labdanum oil, as well as orange-blossom oil, neroli oil, orange-peel oil and sandalwood oil.

As the oil co-component there can be used in principle all natural and synthetic oil components that are suitable for cosmetic use, for example paraffin oils, plant oils (triglyceride oils), liquid waxes, jojoba oil, synthetic fatty acid and fatty alcohol esters, dicarboxylic acid esters, the esters of diols and polyols, linear and branched fatty alcohols and dialkyl ethers.

As the oil co-component for the perfume oil microemulsions there are preferably used, in an amount of at least 0.5% by weight, dialkyl ethers having a total of 12-24 C atoms, so that a preferred clear softener contains from 0.5 to 20, preferably from 1 to 10 and in particular from 1.5 to 7.5% by weight of a perfume-oil microemulsion containing at least 0.5% by weight of a dialkyl ether with a total of 12-24 C atoms as the oil co-component. Mixtures of dialkyl ethers with primary alcohols can also be used as the oil co-component in the perfume oil microemulsions. Preferred herein are clear softeners which contain from 0.5 to 20, preferably from 1 to 10 and in particular from 1.5 to 7.5% by weight of a perfume oil microemulsion containing as the oil co-component a mixture of a dialkyl ether with a total of 12-24 C atoms and a monohydric primary alcohol with 12-36 C atoms.

Although the preparation of perfume oil microemulsions is possible without other co-emulsifiers when a dialkyl ether is used as the oil co-component, it can nonetheless be useful to use a co-emulsifier. Useful as co-emulsifiers are lipophilic nonionic emulsifiers or cationic emulsifiers. As lipophilic nonionic co-emulsifiers there can be used for example fatty acid polyol partial esters of fatty acids with 10-18 C atoms and a polyol with 2-6 C atoms and 2-6 hydroxyl groups. Examples of such co-emulsifiers are for example sorbitan monolaurate, glyceryl monolaurate, methyl glucoside monomyristate, propyleneglycol monopalmitate, as well as the addition products of 1-4 moles of ethylene oxide and such polyol partial esters.

As nonionic emulsifiers for the preparation of the microemulsions there are preferably used alkyloligoglycosides. Alkyloligoglycosides, their preparation and use as surface-active materials are known for example from DE 19 43 689 A1 and DE 38 27 543 A1. Both monoglycosides in which a sugar residue is glycosidically linked to the fatty alcohol, and oligomeric glycosides with an average degree of oligomerisation of up to 2 are useful as the

glycoside group. Useful alkyl oligoglycosides are compounds with the formula  $RO-(G)_x$  wherein RO is the aliphatic linear residue of a primary fatty alcohol with from 8 to 22 and preferably with from 10 to 16 C atoms, and  $(G)_x$  is an oligoglycoside residue with an average degree of oligomerisation x is from 1 to 2. The glucoside group is the glycoside residue that is present in commercially-available alkyloligoglycosides. The weight ratio of perfume oil (A) to alkyl glycoside (C) is preferably in the range from 0.5:1 to 2:1.

The alkylpolyglycoside is used as an emulsifier preferably in amounts of from 1 to 30% by weight. Preferred perfume oil microemulsions have a weight ratio of perfume oil to alkyl polyglycoside in the range of from 0.5:1 to 2:1. A clear softener that is preferred herein contains a perfume oil microemulsion in which the weight ratio of perfume oil to alkylpolyglycoside is from 0.5:1 to 2:, in amounts of from 0.5 to 20, preferably from 1 to 10 and in particular from 1.5 to 7.5% by weight.

Useful cationic co-emulsifiers are for example quaternary ammonium surfactants, for example cetyltrimethylammonium chloride, benzalkonium chloride, distearyl dimethylammonium chloride and in particular readily biodegradable ester quats. As well as the aforesaid quaternary ammonium salts, other known cationic surfactants and emulsifiers can be used herein as co-emulsifiers.

In addition to components a) and b) which will themselves furnish a complete fabric-softener, the compositions of the invention can contain still further ingredients which further improve the application and/or aesthetic properties of the softener. In the invention, preferred compositions contain, in addition to components a) and b), one or more materials from the group comprising electrolytes, non-aqueous solvents, pH regulators, fragrances, perfume carriers, fluorescers, dyes, hydrotropes, suds-inhibitors, silicone oils, anti-redeposition agents, thickeners, enzymes, optical brighteners, anti-greying agents, shrink inhibitors, anti-creasing agents, dye-transfer inhibitors, antimicrobial agents, germicides, fungicides, antioxidants, corrosion inhibitors, antistatic agents, easy-iron agents, water-proofing agents, anti-swelling and antislip agents and UV absorbers.

A great number and variety of salts can be used as electrolytes in the group of inorganic salts. Preferred cations are the alkali and alkaline earth metals, preferred anions are the halides and sulphates. The use of NaCl or  $MgCl_2$  is preferred in the compositions of the invention for manufacturing reasons.

Non-aqueous solvents that can be used in the compositions of the invention for example belong to the group of mono or polyhydric alcohols, alkanolamines and glycol ethers provided they are miscible with water in the stated concentration range. Preferably, the solvents are selected from ethanol, n- or iso-propanol, butanols, glycols, propane or butanediol, glycerol, diglycol, propyl or butyldiglycol, hexylene glycol, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol mono-n-butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, propylene glycol methyl, ethyl or propyl ether, dipropylene glycol methyl or ethyl ether, methoxy, ethoxy, or butoxytriglycol, 1-butoxyethoxy-2-propanol, 3-methyl-3-methoxybutanol, propylene glycol t-butyl ether and mixtures of these solvents.

It can be advantageous to use pH regulators in order to adjust the pH of the compositions of the invention to the desired range. There can be used any known acids or alkalies, provided their use is not prohibited for applications or ecological reasons, or for reasons connected with consumer safety. Generally the amount of these pH regulators will not exceed 1% by weight of the total formulation.

To improve the appearance of the compositions of the invention, these can be dyed with suitable dyes. Preferred dyes, which the skilled worker will have no difficulty selecting, have good storage stability, are inert towards the remaining constituents of the composition and insensitive to light, and they show no marked substantivity to textile fibres so as to avoid colouring them.

As suds-inhibitors useful in the compositions of the invention there can be considered for example soaps, paraffins or silicone oils, which can optionally be applied to carrier materials. Useful anti-redeposition agents, which are also known as soil repellents, are for example

nonionic cellulose ethers such as methyl cellulose and methylhydroxypropyl cellulose with a methoxy group content of from 15 to 30% by weight and a hydroxypropyl group content of from 1 to 15% by weight, calculated on the nonionic cellulose ether, as well as polymers of phthalic acid and/or terephthalic acid known from the art, or their derivatives, in particular polymers of ethylene terephthalates and/or polyethylene glycol terephthalates or anionically and/or nonionically modified derivatives thereof. Especially preferred among these are the sulphonated derivatives of phthalic acid and terephthalic acid polymers.

Thickeners can be added to the compositions of the invention in order to increase viscosity or to improve the thixotropic properties of gels. Thickeners are often also referred to as swelling agents and are usually high-molecular-weight organic materials which can absorb liquids (usually water) and swell to become viscous true or colloidal solutions. Examples of these materials include polyacrylic acids or acrylic acid copolymers for example of the kind available commercially from Goodrich under the trade name Carbopol ®, starch or cationically-modified starch.

As enzymes there can be used in particular materials in the class of hydrolases such as proteases, esterases, lipases or lipolytic enzymes, amylases, cellulases or other glycosyl hydrolases and mixtures of the stated enzymes. In the wash, all of these hydrolases assist in removing stains such as protein, grease or starch-containing stains and built-up soiling. Cellulases and other glycosyl hydrolases can help maintain colour and improve fabric softness by removing pills and microfibrils. Oxireductases can also be used for bleaching or to inhibit dye transfer. Especially useful are enzyme materials obtained from bacteria or fungi, such as *Bacillus subtilis*, *Bacillus licheniformis*, *Streptomyces griseus*, and *Humicola insolens*. Preferably, proteases of the subtilisin type and in particular proteases obtained from *Bacillus lentus* are used. Enzyme mixtures, for example of protease and amylase, or protease and lipase or lipolytic enzymes, or protease and cellulase, or cellulase and lipase or lipolytic enzymes, or protease, amylase and lipase or lipolytic enzymes, or of protease, lipase or lipolytic enzymes and cellulase, and more particularly protease and/or lipase-containing mixtures or mixtures with lipolytic enzymes are of special interest. Examples of lipolytic enzymes are the known cutinases. Peroxidases or oxidases have also been found to be useful

in certain cases. Useful amylases include in particular  $\alpha$ -amylases, iso-amylases, pullulanases and pectinases. As cellulases there are preferably used cellobiohydrolases, endoglucanases and  $\beta$ -glucosidases which are also known as cellobiases, or mixtures thereof. Because different cellulase types differ in their CMCase and avicelase activities, specific mixtures of cellulases can be used to obtain the desired activities. The enzymes can be adsorbed onto carrier materials or embedded in coating materials in order to protect them from premature inactivation. The amount of enzymes, enzyme mixtures or enzyme granules can for example be from about 0.1 to 5% by weight and preferably from 0.12 to about 2% by weight.

Optical brighteners (fluorescers) can be added to the compositions of the invention in order to prevent treated textiles from greying or yellowing. These materials are adsorbed onto the fibres and provide a brightening and simulated bleaching effect by converting invisible UV radiation into visible light of a longer wavelength; UV light absorbed from sunlight is emitted as a bluish fluorescence and produces pure white together with the yellow shade of fabric that has gone grey or yellow. Useful compounds are for example in the class of the 4,4'-diamino-2,2'-stilbenedisulphonic acids (flavone acids), 4,4'-distyryl-biphenylene, methyl umbelliferones, coumarins, dihydroquinolinones, 1,3-diarylpyrazolines, naphthalimides, benzoxazole, benzisoxazole and benzimidazole systems and heterocycle-substituted pyrene derivatives. Optical brighteners are usually present in amounts of from 0.1 to 0.3% by weight on the finished composition.

Anti-redeposition agents are used to keep the soiling that is removed from textile fibres suspended in the wash solution and so to prevent it being redeposited on the fibres. Useful for this purpose are water-soluble usually organic colloids, for example the water-soluble salts of polymeric carboxylic acids, size, gelatine, the salts of ether sulphonics acids, starch or cellulose, or the salts of acidic sulphuric acid esters of cellulose or starch. Water-soluble polyamides containing acid groups are also useful for this purpose. Also useful are soluble starch preparations and starch products other than those mentioned above, for example degraded starches, aldehyde starches and the like. Polyvinylpyrrolidone can also be used. Preferably however there are used cellulose ethers such as carboxymethylcellulose (Na salt), methyl cellulose, hydroxyalkyl cellulose and mixed ethers such as methyl hydroxyethyl

cellulose, methylhydroxy propyl cellulose, methylcarboxy methylcellulose and mixtures thereof in amounts of from 0.1 to 5% by weight, calculated on the compositions.

Because textile fabrics, in particular those consisting of rayon, viscose, cotton and blends thereof, can tend to crease because individual fibres are sensitive to sagging, bending, compression and squeezing transversely to the fibre direction, the compositions of the invention can contain synthetic anti-creasing agents. These include for example synthetic products based on fatty acids, fatty acid esters, fatty acid amides, fatty acid alkylol esters, fatty acid alkylolamides and fatty alcohols that are generally reacted with ethylene oxide, or products based on lecithin or modified phosphoric acid esters.

In order to control microorganisms, the compositions of the invention can contain antimicrobial agents. Depending on the antimicrobial spectrum and the mode of action, these can be either bacteriostats or bactericides, fungistats or fungicides, and so on. Important substances in these groups are for example benzalkonium chlorides, alkylaryl sulphonates, halophenols, and phenol mercuriacetate, although these compounds can equally be omitted from the compositions of the invention.

In order to prevent undesirable changes in the compositions and/or fabrics treated therewith due to the action of oxygen and other oxidative processes, the compositions can contain antioxidants. This class of compounds includes for example the substituted phenols, hydroquinones, pyrocatechols and aromatic amines as well as organic sulphides, polysulphides, dithiocarbamates, phosphites and phosphonates.

Improved wearing comfort can result from the use of antistatic agents added to the compositions of the invention. Antistatics increase the surface conductivity and so enable accumulated charges to be dissipated more easily. External antistatics are usually substances that have at least one hydrophilic molecule ligand and they form a more or less hygroscopic film on surfaces. These usually surface-active antistatics are divided into substances that contain nitrogen (amines, amides, quaternary ammonium compounds), phosphorus (phosphoric acid esters) and sulphur (alkyl sulphonates, alkyl sulphates). External antistatics

are described for example in Patent applications FR 1,156,513, GB 873,214, and GB 839 407. The lauryl (and stearyl)dimethyl benzylammonium chlorides disclosed therein are useful as antistatics for fabrics or as a detergent additive, which additionally provides a textile-finishing effect.

In order to improve the water absorption capacity or wettability of treated fabrics, and to make treated fabrics easier to iron, the compositions of the invention can for example contain silicone derivatives. These also improve the rinsing behaviour of the compositions of the invention, by virtue of their suds-inhibiting properties. Preferred silicone derivatives are for example polydialkyl or alkyl aryl siloxanes in which the alkyl groups contain from 1 to 5 carbon atoms and are completely or partially fluorinated. Preferred silicones are polydimethyl siloxanes which can be derivatised when they have amino functions or are quaternised, or contain Si-OH, Si-H and/or Si-Cl bonds. The viscosities of preferred silicones at 25 °C are in the range between 100 and 100,000 centistokes and the silicones can be used in amounts of between 0.2 and 5% by weight, calculated on the composition as a whole.

Finally, the compositions can also contain UV-absorbers which are held on treated fabrics and improve the light resistance of the fibres. Compounds which have these desired properties are for example compounds that are effective through radiationless inactivation and derivatives of benzophenone with substituents in the 2 and/or 4-position. Also useful are substituted benzotriazoles, 3-phenyl substituted acrylates (cinnamic acid derivatives), optionally with cyano groups in the 2-position, salicylates, organic Ni complexes and natural materials such as umbelliferone and endogenic urocanic acid.

The clear softeners of the invention are manufactured in the known manner by simple mixing of the individual ingredients, the perfume oil microemulsion being prepared separately. Depending on whether other ingredients are added in the form of aqueous solutions or as solids that need to be dissolved, it can be an advantage to add and admix the perfume oil microemulsion last. It is not necessary herein to use high shear forces or the high-energy mixers that are normally needed to produce stable conventional dispersions.

### Examples

A perfume oil microemulsion of the following composition was obtained by thoroughly mixing the components set out in Table 1.

Table 1  
Perfume oil microemulsion [% by weight]

Plantacare ® 220	4.0
Plantacare ® 1200	16.0
Dehyquart AU 46	2.0
Cetiol OE	7.5 <i>~50:50</i>
Perfume	20.0
Water	Balance

Plantacare ® 220: C<sub>8</sub>-C<sub>10</sub> alkyl oligo-(1,5)-glucoside, 63% in water, commercial product ex Henkel, Düsseldorf

Plantacare ® 1200: C<sub>12</sub>-C<sub>16</sub> alkyl oligo-(1,4)-glucoside, 50% in water, commercial product ex Henkel, Düsseldorf

Dehyquart ® AU46: dipalmitoleylethyl-hydroxyethyl-methylammonium methoxy sulphate, 90% in isopropanol, commercial product ex Henkel, Düsseldorf

Cetiol ® OE: Di-n-octyl ether, commercial product ex Henkel, Düsseldorf.

To prepare clear softeners there was used an adipic acid ester quat which had been obtained in accordance with the teaching of DE 195 39 846 (Example 1) and which was used in low-concentration and high-concentration softeners. Softeners E1 and E2 in accordance with the invention and the comparative examples V1 to V4 were fragranced with the same quantities of perfume; the perfume oil microemulsion was used in the examples in accordance with the invention and in the case of the comparative examples, the perfume was incorporated direct. Products E1 and V1 were prepared by stirring the adipic acid ester quat into water heated to 50 °C, stirring for 15 minutes at 50 °C, cooling to 25 °C and then adding the perfume oil microemulsion or perfume. Products E2 and V2 were prepared by stirring the adipic acid ester quat into water heated to 60 °C, adding the emulsifier and solvent, stirring for 15 minutes at 60 °C, cooling to 25 °C and then adding the perfume oil microemulsion or perfume. In order to show that the components that were additionally present in the perfume

oil emulsion were not effective in themselves but only as a microemulsion with the perfume, an emulsifier mixture similar to that used in the perfume oil microemulsion was prepared for comparative examples V3 and V4 and was stirred into the formulation before the perfume oil was added. The composition of the emulsifier mixture is set out in Table 2, and the composition of the products and stability and appearance data are given in Table 3.

Table 2  
Composition of emulsifier mixture [% by weight]

Plantacare 220	13.6
Plantacare 1200	54.2
Dehyquart AU 46	6.8
Cetiol OE	25.4

Table 3  
Composition of softeners [% by weight]

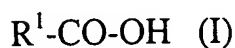
	E1	V1	V3	E2	V2	V4
Adipic acid ester quat*	6.0	6.0	6.0	35.0	35.0	35.0
Perfume	-	0.3	0.3	-	1.5	1.5
Perfume oil microemulsion	1.5	-	-	7.5	-	-
Arylpon F	-	-	-	12.0	12.0	12.0
2-Methyl-2,3-pentanediol	-	-	-	10.0	10.0	10.0
Emulsifier mixture **	-	-	0.44	-	-	2.2
Water	balance	balance	balance	balance	balance	balance
Appearance (after preparation)	clear soln	2 phases	2 phases	clear soln	opaque	opaque
Appearance (after 7 days' storage)	clear soln	2 phases	2 phases	clear soln	2 phases	opaque

\* : 80% in ethanol

Arlypon F : C<sub>12-14</sub> fatty alcohol with 2.5 mol EO

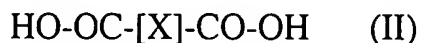
### Claims

1. A clear aqueous softener containing, calculated on the total composition,
  - a) from 2 to 60% by weight of a reaction product of trialkanolamines with a mixture of fatty acids and dicarboxylic acids, the reaction product being optionally alkoxyated and thereafter quaternised in the known manner,
  - b) from 0.5 to 20% by weight of a perfume oil microemulsion with a droplet size between 10 and 100 nm, itself containing from 10 to 50% by weight of perfume oil, from 1 to 10% by weight of an oil co-component, from 1 to 30% by weight of an emulsifier of the alkyl polyglycoside type, and optionally up to 10% by weight of a nonionic or cationic co-emulsifier, the weight ratio of perfume oil to oil co-component being from 10:1 to 2:1, and
  - c) water or an aqueous solution of other active materials and adjuncts to balance.
2. A clear softener according to Claim 1 characterised in that a reaction product of trialkanolamines with a mixture of fatty acids and dicarboxylic acids in a mole ratio of from 1:10 to 10:1 preferably from 1:5 to 5:1 which is optionally alkoxyated and thereafter quaternised in the known manner, is present in the compositions in amounts of from 2 to 60%, preferably from 3 to 35% and in particular from 5 to 30% by weight.
3. A clear softener according to one of Claims 1 or 2 characterised in that it contains a reaction product of triethanolamine.
4. Clear softener according to one of Claims 1 to 3 characterised in that the composition contains a reaction product of triethanolamines with a mixture of fatty acids of formula I



wherein  $R^1\text{-CO-}$  is an aliphatic, linear or branched acyl residue with from 6 to 22 carbon atoms and from 0 and/or 1, 2, or 3 double bonds.

5. A clear softener according to one of Claims 1 to 4 characterised in that the composition contains a reaction product of trialkanolamines with a mixture of fatty acids and dicarboxylic acids of formula II



wherein X is an optionally hydroxyl substituted alkylene group with from 1 to 10 carbon atoms.

6. A clear softener according to one of Claims 1 to 5 characterised in that the composition contains a reaction product of triethanolamine with a mixture of fatty acids and adipic acid in a mole ratio of from 1:5 to 5:1 and preferably from 1:3 to 3:1 which was subsequently quaternised in the known manner.

7. A clear softener according to one of Claims 1 to 6 characterised in that it contains a perfume oil microemulsion containing as the oil co-component a dialkyl ether with a total of 12-24 C atoms in an amount of at least 0.5% by weight, in amounts of from 0.5 to 20, preferably from 1 to 10, and in particular from 1.5 to 7.5% by weight.

8. A clear softener according to one of Claims 1 to 7 characterised in that it contains a perfume oil microemulsion containing as the oil co-component a mixture of a dialkyl ether with a total of 12-24 C atoms and a monohydric primary alcohol with 12-36 C atoms, in amounts of from 0.5 to 20% by weight, preferably from 1 to 10 and in particular from 1.5 to 7.5% by weight.

9. A clear softener according to one of claims 1 to 8 characterised in that it contains a perfume oil microemulsion in which the weight ratio of perfume oil to alkyl polyglycoside is in the range from 0.5: 1 to 2:1.

10. A clear softener according to one of claims 1 to 9 characterised in that in addition to components a) and b) it also contains one or more materials in the group comprising electrolytes, non-aqueous solvents, pH-regulators, fragrances, perfume carriers, fluorescers, dyes, hydrotropes, suds-inhibitors, silicone oils, antiredeposition agents, thickeners, enzymes, optical brighteners, anti-greying agents, anti-shrink agents, anti-crease agents, dye transfer inhibitors, antimicrobial agents, germicides, fungicides, antioxidants, corrosion inhibitors, antistatic agents, easy-iron agents, water-proofing agents, anti-swelling and anti-slip agents as well as UV absorbers.